

any one of claims 2 to 5, wherein the vapor grown carbon fiber is graphitized at a temperature of 2,500°C or more and comprises from 0.1 to 5% by mass of boron.

[Claim 7] A catalyst for polymer electrolyte fuel cell, obtainable by allowing platinum or a platinum alloy to be supported on the electrically conducting carbon composite powder for supporting a catalyst as claimed in any one of claims 1 to 6.

[Claim 8] A polymer electrolyte fuel cell using the catalyst as claimed in claim 7 for the anode and/or cathode electrode.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to an electrically conducting carbon composite powder for supporting a catalyst, more specifically, the present invention relates to a carbon composite powder having good electrical conductivity and useful for supporting a catalyst for use in a fuel cell, particularly, a polymer electrolyte fuel cell, and also relates to a polymer electrolyte fuel cell using the carbon composite powder in the electrode.

[0002]

[Background Art]

In order to cope with recent environmental pollution

issue due to exhaust gas from the internal combustion engine of an automobile or the like, an electric vehicle (EV) is being developed as an alternative in recent years. To keep up with this tendency, a fuel cell is very expected to undertake the power source therefor and a compact and high-performance fuel cell is being demanded.

The fuel cell includes various types of fuel cells such as, according to the kind of electrolytic solution used, alkali type, phosphoric acid type, fused carbonate type and polymer electrolyte type. Among these, a polymer electrolyte fuel cell is attracting an attention as a power source for EV because of its operability at a lower temperature, easy handleability and high output density.

[0003]

For example, Fig. 1 shows a cross-sectional structure of a single cell of a polymer electrolyte fuel cell. The fundamental structure of a single cell is such that an ion exchange membrane 4 containing appropriate water content is disposed in the center and sandwiched by the electrode comprising an anode catalyst layer 3 and a cathode catalyst layer 5. The anode catalyst layer 3 and the cathode catalyst layer 5 each is usually a sheet coated with a paste of carbon powder having supported thereon platinum or platinum alloy powder. The carbon powder is not particularly limited on the kind thereof as long as it has

electrical conductivity, however, those having a specific surface area large enough to support a catalyst are preferred and in general, carbon black is used.

[0004]

In the outer side of each of the anode catalyst layer 3 and the cathode catalyst layer 5, electrically conducting anode gas-diffusing porous sheet 2 and cathode gas-diffusing porous sheet 6 for passing water and gas generated at the reaction are disposed and in the outermost side, a carbon-based separator plate with grooves is disposed to provide reaction gas passages, thereby constructing a single cell. By stacking the single cells to form a multilayer structure, a high-output fuel cell is constructed.

[0005]

Since the reaction of a fuel cell takes place on the catalyst layers, the greatest factor determining the energy amount of a fuel cell is how effectively to use the catalyst. In order to use the platinum catalyst with highest efficiency, the characteristics of carbon as the support have great effect thereon, such as electrical conductivity, adhesion of platinum (supporting property), corrosion resistance against electrolytic solution (ion) and heat conductivity.

[0006]

Furthermore, adhesion as a constituent element of a cell, for example, plane pressure to the ion exchange membrane and the gas diffusion sheet must be maintained over a long period of time.

The entire fuel cell has a structure such that hundreds of single cells are stacked and the whole is cramped up under a predetermined cramping pressure. When the cell is operated over a long period of time, the separator plate, the gas diffusion sheet and the like undertake creeping (a phenomenon that the thickness decreases) and although this creeping amount is small per unit cell, the sum total in the creeping amount of hundreds of cells as a whole is fairly large.

In this meaning, simple carbon black currently used as a support is not only deficient in the electrical conductivity necessary for a high-performance cell but also, when the cell is operated for a long period of time and the plane pressure between respective parts decreases to cause increase in the contact resistance between respective parts, the internal resistance of the cell increases and the cell performance disadvantageously deteriorates.

[0007]

To speak specifically, in the durability test over a time period in excess of ten hundreds of hours, the output

often lowers to the level of 70 to 80%.

[0008]

[Problems to be Solved by the Invention]

The object of the present invention is to develop a catalyst support capable of compensating for the deterioration in the long-term durability of elemental carbon conventionally used as a catalyst support. More specifically, the object of the present invention is to newly create a catalyst support ensuring a higher maximum output, and a catalyst and a cell using the support.

[0009]

[Means to Solve the Problems]

As a result of extensive investigations by taking account of the above-described problems, the present inventors have found that when an electrically conducting carbon composite powder comprising carbon black having mixed therewith fibrous carbon is used as a material for supporting a catalyst in place of the simple carbon black now on use, a catalyst electrode having high output and high durability can be obtained. The fibrous carbon is preferably vapor grown carbon fiber.

In the carbon composite powder, the vapor grown carbon fiber is preferably mixed in an amount of 1 to 7% by mass.

The carbon black is preferably carbon black heat-treated and graphitized at a temperature of 2,500°C or more.

The carbon black preferably comprises from 0.1 to 5% by mass of boron, so that the graphitization degree can be more increased.

Similarly, the vapor grown carbon fiber mixed is preferably vapor grown carbon fiber comprising from 0.1 to 5% by mass of boron and heat-treated at a temperature of 2,500°C or more, so that the electrically conductivity can be more elevated.

A catalyst for a polymer electrolyte fuel cell is produced using this composite powder for supporting a catalyst and platinum or a platinum alloy as main raw materials and the catalyst is used for the anode catalyst layer and/or the cathode catalyst layer, whereby a polymer electrolyte fuel cell having high output and high durability can be obtained.

[0010]

[Mode for Carrying Out the Invention]

The present invention is described in detail below.

The present invention relates to the capability when a composite powder of carbon and carbon fiber as a collector such as a catalyst support for a fuel cell. The effect of the present invention is brought out particularly when the composite powder is used as a support in the catalyst layer of a polymer electrolyte fuel cell.

[0011]

The carbon black for use in the composite powder of the present invention is commercially available carbon black usually having an average primary particle size of 1  $\mu\text{m}$  or less and includes, according to the production process, oil furnace black obtained by incompletely combusting aromatic hydrocarbon oil, acetylene black obtained by completely combusting and thereby thermally decomposing acetylene, thermal black obtained by completely combusting natural gas, and channel black obtained by incompletely combusting natural gas. Any of these can be used.

In particular, oil furnace black and acetylene black are preferred. The reasons therefor is as follows. One of important factors determining the performance of carbon black as an electrically conducting material is a primary particle chain (aggregation structure) called structure. This aggregation structure is generally a structure of carbon black, where fine spherical primary particles gather and form irregular chained branches. As the number of primary particles is larger and as the chained branches are more complicated (called high structure state), the effect of imparting electrical conductivity is higher.

This high structure state can be easily formed in the oil furnace black and acetylene furnace black and therefore,

these carbon blacks are preferred.

[0012]

The fibrous carbon for use in the present invention may be any of those called PAN-type or called pitch-type, those obtained by the vapor phase process, and those called nanotube having a size on the order of nanometer, however, vapor grown carbon fiber heat-treated and thereby enhanced in the electric conductivity is preferred because of its appropriate elasticity.

The vapor grown carbon fiber (hereinafter simply referred to as "VGCF") is produced by thermally vapor-phase decomposing a gas such as hydrocarbon, in the presence of a metal-based catalyst.

Examples of the production method include a method where an organic compound such as benzene is used as a starting material, an organic transition metal compound such as ferrocene is used as a metal-based catalyst, and these are introduced together with a carrier gas into a reaction furnace to produce VGCF on a substrate (see, JP-A-60-27700 (the term "JP-A" as used herein means an "unexamined published Japanese patent application")), a method where VGCF is produced in the suspension state (see, JP-A-60-54998), and a method where VGCF is grown on a reaction furnace wall (see, Japanese Patent 2,778,434).

In JP-B-3-64606 (the term "JP-B" as used herein means



an "examined Japanese patent publication"), a metal-containing particle previously supported on a refractory support such as alumina or carbon, is contacted with a carbon-containing compound at a high temperature to obtain VGCF of 70 nm or less.

VGCF produced by any of these methods can be used in the present invention.

[0013]

VGCF constituting the present invention suitably has a fiber diameter of 20 to 300 nm and a fiber length of less than 100  $\mu\text{m}$ . This VGCF is mixed with carbon black to occupy from 1 to 7% by mass of the entire powder.

The diameter of VGCF is preferably 20  $\mu\text{m}$  or more because if the diameter is less than 20  $\mu\text{m}$ , the VGCF can be hardly mass-produced in industry, which is not practical, and due to the fineness, the handling is cumbersome but the effect is not so high. On the other hand, if the diameter exceeds 300  $\mu\text{m}$ , the fibers are poorly entangled for the particle size or shape of carbon black and the effect on the electrical conductivity cannot be obtained by the addition.

If the fiber length exceeds 100  $\mu\text{m}$ , the fibers cannot be uniformly blended with carbon black and the effect as a composite powder can be hardly obtained.

The vapor grown carbon fiber takes a branched

structure in many cases. In this case, the fiber length means a length from a branch point of a branch to the distal end or to the next branch point.

If the amount of VGCF added is less than 1% by mass, the addition effect can be hardly obtained, whereas if it exceeds 7% by mass, the ratio of carbon black as a support on which a platinum catalyst is supported, decreases and the cell characteristics are reduced.

[0014]

The pitch-type carbon fiber and PAN-type carbon fiber have a fiber length in excess of 100  $\mu\text{m}$  and each fiber as it is cannot be uniformly blended with carbon black. Furthermore, on taking account of the electrical conductivity, VGCF is preferred.

[0015]

In the present invention, the carbon black is preferably heat-treated at a temperature of 2,500°C or more, more preferably heat-treated in the state of the carbon black being mixed with a boron compound such as boron carbide, boron oxide or boron nitride, at 2,500°C or more in a non-oxidative atmosphere such that the carbon black comprises from 0.1 to 5% by mass of boron.

By heat-treating the carbon black at 2,500°C or more, not only high electrical conductivity is attained but also the characteristics such as chemical stability and heat

conductivity are improved and when this carbon black is used as a catalyst support of a fuel cell, the power generation efficiency (power generated per unit volume) is improved and the durability (the ratio of maximum output after the continuous use for 1,000 hours or more, to the initial maximum output) is also improved.

Particularly, in the case of carbon black elevated in the crystallinity by the heat-treatment at 2,500°C or more, these improvements on the characteristics of a cell are remarkable. For this purpose, the crystallinity is elevated in the present invention by the addition of boron as means for elevating graphitization crystallinity.

The incorporation of boron can be attained by mixing a boron compound and carbon black, and heat-treating the mixture.

The boron compound and carbon black may be mixed by any method without using any special machine as long as these can be uniformly mixed.

The heat-treatment furnace may be any furnace as long as the heat-treatment can be performed at a desired temperature and, for example, an Acheson furnace, a high frequency furnace and a furnace using a graphite heating element may be used.

The non-oxidative atmosphere can be obtained, in the case of Acheson furnace, by burying the material to be

heated in the carbon powder and in the case of other furnaces, by purging the atmosphere with an inert gas such as nitrogen or argon, according to the necessity.

The heat-treatment time is not particularly limited as long as the time period is long enough for the heated material as a whole to reach a predetermined temperature.

[0016]

VGCF is usually used by burning it at a temperature around 1,000°C after the production. However, when VGCF used is heat-treated in the same manner as the carbon black, particularly, mixed with a boron compound and then heat-treated, the VGCF can have improved electrical conductivity and in a cell manufactured, can improve as a catalyst the characteristics (power generation efficiency, durability) of the cell.

[0017]

The boron compound used here may be any as long as a desired boron content can be obtained after the heat-treatment, however, in view of easy availability and workability, the boron compound is preferably an inorganic compound, more preferably boron carbide.

The amount of the boron compound added before the heat-treatment must be in excess of the target content because boron may be volatilized out depending on the heat-treatment conditions.

[0018]

By mixing from 1 to 7% by mass of VGCF with carbon black and using the mixture as the powder for supporting a catalyst in the catalyst layer, the cell can be greatly improved in the characteristics. In the mixing, the powder is uniformly mixed using a continuous system mixer such as screw feeder and cycle feeder, or a batch-system mixer such as mixing roll and banbury mixer.

[0019]

The carbon black and VGCF may also be previously mixed before the heat-treatment and then heat-treated. At this time, the above-described boron compound may also be previously added and heat-treated. In these heat-treatments, the same effect can be obtained.

[0020]

Platinum or a platinum alloy may be supported on the composite powder by the method described below or the like. The composite powder is mixed and added to an ethanol solution having dissolved therein, for example, chloroplatinic acid hexahydrate, the resulting solution is evaporated to dryness on a hot plate while stirring to obtain platinum compound-supported powder, this platinum compound-supported powder is added to a hydrazine monohydrate solution, and the mixture is stirred, washed with ion exchanged water and dried to obtain metal

platinum-supported powder.

To a mixture of this platinum-supported powder and ion exchange resin or a mixture of this platinum-supported powder, ion exchange resin and water-repellent resin, distilled water or a solvent is added and thoroughly stirred in a ball mill or the like to form a paste. This paste is coated on a carbon paper and dried at a temperature sufficiently high to thoroughly volatilize the solvent and the formed layer can be used as a catalyst layer.

Examples of the ion exchange resin include perfluorocarbon resin having, as the ion exchange group, a sulfonic acid group or a carboxylic acid group. Examples of the water-repellent resin include polytetrafluoroethylene.

[0021]

[Examples]

The present invention is described in greater detail below by referring to the Examples.

As the carbon black, the following powder samples were prepared.

(1) Heat-Untreated Product

Acetylene black (Denka Black, trade name) produced by Denka K.K. was used as a sample as it is. This is hereinafter simply referred to as KCB.

## (2) Graphitization Heat-Treated Product

Furnace black (Showa Black, trade name) produced by Showa Cabot K.K. was filled in a graphite-made crucible and burned at respective temperatures of 2,500°C and 2,700°C in an Acheson furnace over 10 days to prepared samples different in the treatment temperature. This heat-treated carbon black is hereinafter simply referred to as GrCB.

## (3) Graphitization Heat-Treated Product Comprising Boron

Furnace black produced by Showa Cabot K.K. and previously pulverized boron carbide powder produced by Denka K.K. were mixed, filled in a graphite-based crucible and burned at respective temperatures of 2,500°C and 2,700°C to prepare samples different in the treatment temperature. After the heat-treatment, the boron content of each sample was confirmed by the chemical analysis. This heat-treated carbon black comprising boron is hereinafter simply referred to as B-GrCB.

[0022]

As the vapor grown carbon fiber, vapor grown carbon fibers (VGCF, trade name) produced by Showa Denko K.K. having a diameter size of 30 nm, 50 nm, 100 nm, 200 nm and 300 nm were prepared.

As a result of observation through SEM, these all had a fiber length of less than 100  $\mu\text{m}$  and all showed a branched structure form.

These fibers were individually burned in a non-oxidative atmosphere, subjected to the same graphitization heat-treatment as the carbon black, or heat-treated after mixing the fiber in a screw feeder with the above-described boron carbide produced by Denka K.K. which had been pulverized. Thus, various samples of vapor grown carbon fiber were produced under the conditions shown in Table 1.

The boron content was confirmed by chemical analysis.

In the following, the boron-containing VGCF is simply referred to as B-VGCF.

[0023]

[Table 1]

Conditions in Production of Vapor Grown Carbon Fiber Sample

Sample No.	Heat-Treatment Temperature (°C)	Fiber Size (nm)	Boron Content (mass%)
VGCF 1	1200	300	0
VGCF 2	1200	200	0
VGCF 3	1200	30	0
VGCF 4	2800	300	0
VGCF 5	2800	200	0
VGCF 6	2800	50	0
B-VGCF 1	2500	200	0.5
B-VGCF 2	2500	200	3
B-VGCF 3	2500	200	7
B-VGCF 4	2700	300	5
B-VGCF 5	2700	200	0.5
B-VGCF 6	2700	100	3



[0024]

Using each of these samples, a catalyst layer was formed as follows and then, as shown in Fig. 1, a single cell of a polymer electrolyte fuel cell was manufactured and evaluated on the cell characteristics.

In a ball mill, 1.5 g of carbon black having supported thereon 30% by mass of platinum or 1.5 g of composite powder of the carbon black and VGCF (see, Table 2) having supported thereon 30% by mass of platinum, 10 g of a 5% concentrated solution of ion exchange resin (Nafion, trade name, produced by Du Pont) and 5 g of distilled water were mixed for 30 minutes to obtain a paste. This paste was coated on a gas diffusion layer comprising carbon sheet (ST sheet, trade name, produced by Showa Denko K.K.) treated with 30% by mass of water-repellent resin polytetrafluoroethylene. Subsequently, the paste was dried at 60°C for 10 minutes and heated at 130°C under a pressure of 200 N/cm<sup>2</sup> for 1 minute to manufacture a gas diffusion electrode in which a catalyst layer supporting platinum corresponding to 1 mg/cm<sup>2</sup> was formed.

[0025]

As shown in Fig. 1, two pairs of the thus-manufactured electrode (one is anode catalyst layer 3/anode gas diffusion porous sheet 2 and another is cathode catalyst layer 5/cathode gas diffusion porous sheet 6) and a

separator plate 1 were disposed to oppose each other with intervention of an ion exchange membrane (Nafion, trade name, produced by Du Pont) 4 and thereby constitute a single cell of a polymer electrolyte fuel cell.

This single cell was operated using hydrogen as the fuel gas while passing an oxidizing gas (air) under an applied pressure of 10 N/cm<sup>2</sup>, and the cell characteristics of a polymer electrolyte fuel cell were evaluated.

For the evaluation of durability, a continuous operation was performed at an output of 0.3 W/cm<sup>2</sup> for 4,000 hours and the output retention (a ratio of the output after the operation for 4,000 hours to the output at the initiation of operation) was determined.

The blending conditions between carbon black and VGCF, and the evaluated cell characteristics (maximum output, retention) of a single cell employing a catalyst using the carbon black and VGCF are shown in Table 2.

[0026]

[Table 2]

Blending Ratio of Composite Powder and Characteristics of Single Cell Battery Using the Composite Powder

	Production Conditions and Blending Ratio of Composite Powder						Characteristics of Single Cell	
	Carbon Black			VGCF		Blending Ratio	Maximum Output, W/cm <sup>2</sup>	Durability, %
	Kind	Heat-Treatment Temperature, °C	Boron Content, mass%	Kind	Boron Content, mass%	Amount of VGCF Added, mass%		
Example 1	KCB	-	-	VGCF 1	-	5	0.43	93
Example 2	KCB	-	-	VGCF 4	-	5	0.45	95
Example 3	KCB	-	-	B-VGCF 1	0.5	3	0.42	98
Example 4	KCB	-	-	B-VGCF 4	5	3	0.46	97
Example 5	GrCB	2500	-	VGCF 3	-	7	0.45	93
Example 6	GrCB	2700	-	VGCF 4	-	7	0.49	96
Example 7	GrCB	2500	-	B-VGCF 2	3	4	0.50	97
Example 8	GrCB	2700	-	B-VGCF 5	0.5	4	0.49	98
Example 9	B-GrCB	2500	3	VGCF 1	-	2	0.51	93
Example 10	B-GrCB	2700	0.5	VGCF 5	-	2	0.47	98
Example 11	B-GrCB	2500	5	B-VGCF 3	7	1	0.49	97
Example 12	B-GrCB	2700	7	B-VGCF 6	3	1	0.48	98
Comparative Example 1	KCB	-	-	-	-	-	0.11	73
Comparative Example 2	GrCB	2700	-	-	-	-	0.28	81
Comparative Example 3	B-GrCB	2700	7	-	-	-	0.32	85

[0027]

[Effects of the Invention]

Although simple carbon black has been heretofore used as a catalyst support in a polymer electrolyte fuel cell, according to the present invention, the composite powder of the present invention is used as the support and a catalyst layer mainly comprising a mixture of this composite powder and platinum or a platinum alloy is used for the electrode, whereby the power generation efficient is greatly elevated and also the long-term durability over ten hundreds of hours is enhanced.

[BRIEF DESCRIPTION OF DRAWING]

[Fig. 1]

Fig. 1 is a cross-sectional view showing the fundamental structure of a single cell of a polymer electrolyte fuel cell, using the composite powder of the present invention for the catalyst layer.

[Description of Numerical References]

- 1 separator plate with grooves
- 2 anode gas diffusing porous sheet
- 3 anode catalyst layer
- 4 ion exchange membrane
- 5 cathode catalyst layer
- 6 cathode gas diffusing porous sheet